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[54] **Invention Title:** Method for preparing Ag catalyst for ethylene epoxidation

[57] Abstract

The invention refers to a process for preparing silver catalyst used for epoxidizing ethylene. It mainly solves the defects located at Ag catalysts made by previous preparative technologies, i.e., those catalysts having no high enough activity yet. In the invention alpha-alumina is treated as carrier by the solution or gas of alkaline substance. The amount of alkaline substance is 0.01 ~ 500% by weight percentage of the carrier, with treatment temperature of 30 ~ 800 °C and treatment duration of 1 ~ 30 hours. The carrier treated with alkaline substance is washed with water until it becomes neutral, drying to obtain carrier, and carrying silver and at least one kind of assistant chosen from S, Re, Mo, W, Ni, alkali metal, and alkali-earth metal. The loading amount of Ag is 5 ~ 40% of catalyst weight as counted by Ag, and the loading amount of assistant is 0.001 ~ 1% of catalyst weight as counted by element weight. The Ag catalyst prepared in the invention for production of EO has the advantages of low reaction temp, high activity and high selectivity at the same time. It can be used in industrial production of Ag catalyst for EO production.

1. A kind of preparative method of Ag catalyst for ethylene epoxidation includes the following steps:
 - a) With $\alpha\text{-Al}_2\text{O}_3$ as carrier, the carrier amount is 60 ~ 94% of catalyst weight.
 - b) The carrier is treated by the solution or gas of alkaline substance. The amount of alkaline substance accounts for 0.01 ~ 500% by weight percentage of the carrier, with treatment temperature of 30 ~ 800 °C and treatment duration of 1 ~ 30 hours. The carrier treated with alkaline substance is washed with water until it becomes neutral, drying to obtain carrier of Ag catalyst.
 - c) Ag is loaded to the carrier obtained in step b), with the loading amount of Ag accounting for 5 ~ 40% of catalyst weight as counted by Ag.
 - d) Assistant catalyst is loaded before, during or after the Ag loading, and the assistant catalyst can be one or a mixture of which are chosen from S, Re, Mo, W, Ni, alkali metal, and alkali-earth metal. The loading amount of assistant is 0.001 ~ 1% of catalyst weight as counted by element weight.
2. According to the preparative method of Ag catalyst for ethylene epoxidation stated in Claim 1, wherein the alkaline substance contains inorganic alkaline compounds, organic alkaline compounds or their mixtures.
3. According to the preparative method of Ag catalyst for ethylene epoxidation stated in Claim 2, wherein the inorganic alkaline compounds can be the oxides, hydroxides, weak acid salts or their mixtures of alkali metals or alkaline earth metals.
4. According to the preparative method of Ag catalyst for ethylene epoxidation stated in Claim 2, wherein the inorganic alkaline compound is NH_3 , which can be ammonia water, NH_3 gas, a mixture of NH_3 gas and air or a mixture of NH_3 gas and nitrogen.
5. According to the preparative method of Ag catalyst for ethylene epoxidation stated in Claim 2, wherein organic alkaline compounds can be amines compounds, pyridine compounds or their mixtures.
6. According to the preparative method of Ag catalyst for ethylene epoxidation stated in Claim 2, wherein the dosage of alkaline material is 0.05 ~ 300% of carrier by weight percentage.
7. According to the preparative method of Ag catalyst for ethylene epoxidation stated in Claim 3, wherein in the treatment temperature is 50 ~ 500 °C and the treatment duration is 2 ~ 20 hours.
8. According to the preparative method of Ag catalyst stated in Claim 1, wherein the alkali metals are Li, Na, K or Se and alkaline earth metals are Mg or Ca.
9. According to the preparative method of Ag catalyst for ethylene epoxidation stated in Claim 1, wherein fluorochemicals is added into the raw material in preparation of step a), and the amount of fluorochemicals is 0.01 ~ 20% of weight of Al_2O_3 as counted by F, followed by kneading, shaping and calcinations.

Method for preparing Ag catalyst for ethylene epoxidation

Technology field

The invention refers to a kind of preparative method of Ag catalyst for ethylene epoxidation.

Background techniques

The use of Ag catalyst in EO industrial production by ethylene epoxidation has been widely applied in industrial equipments. High activity and selectivity are the two important properties of Ag catalyst, while performance of carrier plays an important role in catalyst activity and selectivity. Ag catalyst is usually prepared by α - Al_2O_3 as carrier, Ag as main active composition and a small addition of assistant catalyst. High active catalyst requires large Ag particle specific surface and large enough specific surface of carrier. However, if the specific surface is too large, it would bring out the problem of difficulty in heat dissipating of the reaction system, sharply promote deep oxidation and reduce the selectivity of product EO. To adjust the relationship between the activity and selectivity of catalyst so as to make the catalysts have both high activity and high selectivity at the same time, has been a key point of attention and research for a long time. In the present technologies, many patents refer to the Ag catalysts and catalyst carriers for EO production. However, although the Ag catalysts and carrier designed presently have been improved adequately with relatively high activity and selectivity, given the EO production scale, even slight improvements of the activity and selectivity of catalyst would bring very high economic benefit. As a result, there is still a demand for developing Ag catalyst with higher activity and selectivity in present technologies.

US4742034 introduces a kind of preparative method of Ag catalyst for ethylene epoxidation reaction, wherein Al_2O_3 with rich alkali metal is taken as carrier; alkali metals mainly in the form of fluoride or nitrate and F are added into the main body. The catalyst has relatively good selectivity and stability and the selectivity of catalyst containing F reaches to 81.2%, which is 2% higher than that of catalyst without F.

EP716884A₂ introduces a kind of preparative method of Ag catalyst. Alkali metal is pre-soaked into the carrier, after heat treatments, it is loaded to the carrier, then the main body soaks Ag, Re, S, alkali metals etc. The aim of the pretreatment of carrier is to improve the initial selectivity and the stability of selectivity. With the prepared catalyst in this way used in ethylene epoxidation reaction, the selectivity can reach to 82% with long and stable selectivity.

Chinese patent 95196582.4 (CN1168644A) provides a kind of preparative method of catalyst for epoxidation of ethylene to EO, wherein inert carrier is soaked into a kind of Ag/amine solution, after calcinations, Cs, Re, S etc assistant catalysts are brought in and they are calcinated at 100 °C above in inert gas. Material mixture composed of 7% O_2 (V), 8% CO_2 , 15% C_2H_4 , 70% N_2 goes through catalyst at the air speed of 5500h^{-1} , with the reaction pressure 21.69P. When the eluting concentration of EO is 1.5% (volume), the reaction temperature indicating the activity of catalyst activity is 228 ~ 259 °C, with the selectivity of 81 ~ 83.7%.

Chinese patent 00119774.6 introduces a kind of preparative method of catalyst carrier. Fluorochemical is added into the Al_2O_3 raw material, after calcinations at high temperature, $\alpha\text{-Al}_2\text{O}_3$ is generated. Then it is kneaded and shaped with the additives e.g. pore-making agent, luting agent etc, through the second calcinations at high temperature, $\alpha\text{-Al}_2\text{O}_3$ carrier is made. If Ag catalyst prepared by the carrier is applied in ethylene epoxidation to EO has relatively high selectivity; however reaction activity of the catalyst is not high enough. In the condition of 2.1 MPa reaction pressure and 7000h^{-1} air speed, when the EO concentration at the reactor outlet is 1.4 mol%, the reaction temperature indicating the activity of catalyst activity is $225 \sim 230\text{ }^\circ\text{C}$.

The abovementioned catalysts have relatively good selectivity, activity and stability, but reaction activity of the catalyst is not high enough.

Invention content

The technical problem to be solved in the invention is to overcome the defect of low reaction activity located at Ag catalysts prepared by the present documents and to provide a kind of preparative method of Ag catalyst for ethylene epoxidation. If the catalyst prepared in this way is applied in ethylene epoxidation reaction for EO production, it has the advantages of low reaction temperature and high reaction activity, and at the same time, high selectivity of catalyst is kept.

In order to solve the above technical problems, the following technical plans are adopted in the invention: a kind of preparative method of Ag catalyst for ethylene epoxidation includes the following steps by turns:

- a) With $\alpha\text{-Al}_2\text{O}_3$ as carrier, the carrier amount is 60 ~ 94% of catalyst weight.
- b) The carrier is treated by the solution or gas of alkaline substance. The amount of alkaline substance accounts for 0.01 ~ 500% by weight percentage of the carrier, with treatment temperature $30 \sim 800\text{ }^\circ\text{C}$ and treatment duration 1 ~ 30 hours. The carrier treated with alkaline substance is washed with water until it becomes neutral, drying to obtain carrier of Ag catalyst.
- c) Ag is loaded to the carrier obtained in step b), with the loading amount of Ag accounting for 5 ~ 40% of catalyst weight as counted by Ag.
- d) Assistant catalyst is loaded before, during or after the Ag loading, and the assistant catalyst can be one or a mixture of which are chosen from S, Re, Mo, W, Ni, alkali metal, and alkali-earth metal. The loading amount of assistant is 0.001 ~ 1% of catalyst weight as counted by element weight.

In abovementioned technical plans, aluminum hydroxide, transient phase aluminum oxide or mixture of the two are used as material in $\alpha\text{-Al}_2\text{O}_3$ carrier preparation. Taking the cost of raw material into consideration, the optimal raw material of aluminum oxide is aluminum hydroxide, which can be one of alumina monohydrate, pseudo alumina monohydrate, alumina trihydrate or amorphous alhydrogel, or a mixture of two or above kinds of them, alumina monohydrate, alumina trihydrate or the mixture of the two are the optimal choices.

Due to fluoride is favorable for forming Al_2O_3 into $\alpha\text{-Al}_2\text{O}_3$ crystal in calcinations and remove the unnecessary micropores, and selectivity of catalyst is improved as carrier. In the preparation of $\alpha\text{-Al}_2\text{O}_3$ carrier in the invention, luting agent, pore-making agent and water are added into the Al_2O_3 raw material, at the same time, a kind of fluorochemical can be added non-compulsorily and then the mixed material is obtained,

wherein the addition amount of fluorochemical is 0.01 ~ 20% of Al_2O_3 weight as counted by F, the addition amount of luting agent is 0.01 ~ 10% of Al_2O_3 weigh, and the addition amount of pore-making agent is 5 ~ 50% of Al_2O_3 . The fluorochemicals used include alkali metal fluoride, alkaline earth metal fluoride, NH_4F , $(\text{NH}_4)\text{HF}_2$, AlF_3 or HF etc, NH_4F , wherein HF or AlF_3 are the optimal choices. The luting agents include nitric acid, alhydrogel, inorganic slime, French chalinoplasty, calcium-silicate, barium-silicate, barium aluminate, cellulose, methyl-, ethyl- or carboxyethyl cellulose, methyl stearate or ethyl stearate, waxes, poly-alkylene oxide etc. Proper pore-making agent includes carbon-containing material such as coke, carbon powder, graphite; powder plastics such as polyethylene, polystyrene, polycarbonate, rosin; cellulose and cellulose series of material; sawdust and other plant material such as powder hard shells e.g. carya shell, walnut shell and hazelnut shell etc.

After the abovementioned mixed material is fully kneaded, it is made into certain shape, the carrier shape can be globular, mass, pill, cylinder, rasching, porous cylinder, clover etc. The above shaped carrier is dried at 60-200 °C, and through calcinations at high temperature, $\alpha\text{-Al}_2\text{O}_3$ treated with F or not is acquired. The stated calcination temperature is 1000 °C ~ 1700 °C and the optimal range is 1200 °C ~ 1600 °C, and the better range is 1300 °C ~

1500 °C. The calcination duration is 0.5 ~ 20 hours, the optimal range is 1 ~ 10 hours, and the better range is 1 ~ 6 hours. Sometimes, the method for mixing $\alpha\text{-Al}_2\text{O}_3$ powder with different particle size is used to control the pore distribution of the carrier.

After fluoridizing treatment, through calcinations at high temperature, the Al_2O_3 has sheet-shape crystal structure. The width of sheet-shape crystal can be controlled at 0.1-30 μm by selecting proper initial Al_2O_3 raw material and proper addition amount of fluorochemical, wherein the optimal range is 0.5 ~ 10 μm , and the thickness is 0.1 ~ 4 μm , with the optimal range 0.1 ~ 2 μm .

The prepared $\alpha\text{-Al}_2\text{O}_3$ carrier (including fluoridizing treatment or without fluoridizing treatment) should be treated with alkaline substance. The used alkaline substance includes all the compound which can be prepared into alkalic solution and alkalic gases, such as inorganic alkalic compounds, organic alkalic compounds or their mixtures, among them, inorganic alkalic compounds can be the oxides of alkali metal or alkaline earth metal, hydroxide, the weak acid salts of alkali metal or alkaline earth metal, such as carbonate, acetate, oxalate, carboxylic salt or their mixtures, the optimal alkali metals are Li, Na, K or Cs, and the optimal alkaline earth metal is Mg or Ca. The inorganic alkalic compounds can be ammonia, which has ammonia water and NH_3 gas two material states. The organic alkalic compounds can be amine compounds, pyridine compound or their mixtures, wherein amine compounds can be ethanediamine, cholamine, methylamine, ethylamine, amidobenzene or their mixtures, the optimal choice is ethanediamine, cholamine or their mixture, and pyridine compounds can be pyridine, and trimethyl pyridine etc. The amount of alkaline substance is 0.01 ~ 500% as counted by weight percentage of the carrier, and the optimal choice is 0.05 ~ 300%. The treatment temperature is 30 ~ 800 °C, the optimal choice is 50

~ 500 °C, and the better choice is 80 ~ 400 °C. The treatment duration is 1 ~ 30 hours; the optimal choice is 2 ~ 20 hours. Normally, the higher the treatment temperature is, the shorter the treatment duration is.

Alkali treatment may adopt solution or gas of alkaline substance. When it is treated by alkaline substance solution, the preparation of solution is to dissolve 0.01 ~ 500% of carrier weight of alkaline substance into water, methanol, ethanol, and acetone or chloroform etc solvents as counted by carrier weight percentage, wherein the optimal solvent is water or ethanol, to make the prepared solution volume being able to fully soak the carrier at least. The volume ratio of solution to carrier can be 0.1 ~ 20: 1, and the optimal choice is 1 ~ 5: 1.

The detailed alkaline substance solution can be LiOH aqueous solution, NaOH-methanol solution, KOH aqueous solution, CsOH-ethanol solution, ammonia water, Na_2CO_3 aqueous solution, ethanediamine, cholamine, pyridine or trimethyl pyridine etc. When it is treated with gases of alkaline substance, the gases can be NH_3 gas, the mixture of NH_3 gas and air or the mixture of NH_3 gas and nitrogen, among them, molar ratio of air (nitrogen): NH_3 gas is 0 ~ 10: 1, to make gas passes through the carrier bed layer at a certain speed with treatment duration of 1 ~ 30 hours. The introduced amount of alkalic gas is 0.01 ~ 500% as counted by carrier weight percentage.

The treated carrier is washed for several times by water which may be distilled water or deionized water until the eluting liquid after washing is neutral, drying at 80 ~ 200 °C, and then obtaining the Ag catalyst carrier for EO

production. The carrier acquired through the above method, its specific surface area is usually 0.2 ~ 1.5 m^2/g , the absorption rate is usually 0.2 ~ 0.8 ml/g, and the bulk specific gravity is 0.4 ~ 1.0 g/ml.

There are many ways to load Ag to the carrier treated with alkaline substance during the preparation of the catalyst in this invention. One way is to soak the carrier with AgNO_3 aqueous solution, and then reduce the Ag^+ into metal Ag with hydrogen, hydrazinium or methanal; another way is to soak carrier with the ammonia water of silver oxalate or silver carbonate, drying and reducing the Ag^+ into metal Ag. The optimal method is to soak the carrier with the mixture of a certain Ag salt-organic solvent/reductant-water, after that, reducing Ag^+ into metal Ag through heat treatment. This method can load the metal Ag to the carrier in the form of highly dispersing thin particle shape.

As the mixture of Ag salt-organic solvent/reductant-water, the Ag salt includes inorganic salt and organic salt e.g. AgNO_3 , Ag_2CO_3 , Ag_2SO_4 , AgCl , silver oxalate, silver acetate, silver lactate, silver succinate, and silver oxyacetate, and the optimal choice is silver oxalate. Organic solvent/reductant can not only be used as the solvent for Ag salts, but also reduce the ionic Ag into the metal Ag at the circumstance of heating. Organic amines, especially the alkanolamine, alkylidene diamine e.g. ethanediamine, propanediamine, cholamine, propanolamine and their mixture or the mixture with ammonia amine, can be adopted. Usually, there are two preparative methods for Ag-soaking solution, which can be explained through the following two examples. One example is that Ag_2O reacts with the mixture of ethanediamine and oxalic acid to generate a kind of mixture containing silver oxalate-ethanediamine as Ag-soaking solution. Be sure to avoid directly putting Ag_2O into ethanediamine, because the generated Ag-ethanediamine solution is not stable and easy to cause explosion. The other example is that AgNO_3 solution and ammonium oxalate aqueous solution are mixed to generate silver oxalate sediment. The acquired sediments are washed by water for several times to remove the NO_3^- , then ethanediamine aqueous solution is used to dissolve silver oxalate sediment, and the acquired silver oxalate-ethanediamine mixture can be used as Ag-soaking solution.

The carrier is taken out from Ag soaking solution, dried, and conducted with heat treatment. Hot gas goes through wet carrier, and removes the organic solvent and water in wet carrier; at the same time, Ag deposits on the carrier in the form of metal thin particle. The loading amount of Ag is 5 ~ 40% of catalyst weight, and the optimal choice is 10 ~ 20%. The heat-treatment gases can be air, nitrogen, oxygen, hydrogen, CO_2 , steam or their mixture. The

heat-treatment temperature can be 80 ~ 700 °C, and the optimal choice is 150 ~ 500 °C. The heat-treatment duration can be 1 ~ 10 hours, and the optimal choice is 2 ~ 30 minutes.

Assistant catalyst can effectively improve the catalyzing performance such as selectivity, activity, stability etc. The assistant in the invention is selected from one of S, Re, Al, Wu, Ni, alkali metal, alkaline earth metal or their mixture, and the optimal choice is S, Re, alkali metal or their mixture. The loading amount of assistant catalyst is 0.001 ~ 1% of catalyst weight as counted by the element weight, and the optimal choice is 0.03 ~ 0.1%. Among them, alkali metal is the most common assistant catalyst and Cs is the best. The proper alkali metal assistant catalyst materials are: nitrate of alkali metal, hydroxide, carbonate, oxalate, carboxylic salt, alkoxide or their mixture, the detailed examples are Cs_2CO_3 , Rubidium Nitrate, KOH, sodium acetate and lithium oxalate. Assistant catalyst can be loaded to carrier before, during or after the loading of Ag into carrier.

The catalyst prepared by this invention is applied in the reaction of ethylene with oxygen molecules to produce EO. The adopted technical conditions are similar with those recorded in common documents. The available conditions for Ag catalyst in this invention are: the reaction temperature is 150 ~ 300 °C, with the optimal choice

200 ~ 300 °C; reaction pressure should be 10-40kg/cm², with the optimal choice 15 ~ 30 kg/cm²; the air space rate is 1000-30000h⁻¹, with the optimal choice is 3000-15000h. The composition of raw material gases can be 0.5 ~ 40% ethylene, 3 ~ 10% oxygen, 5 ~ 30% CO₂ and few inhibitor, the others are inactive gases such as nitrogen, NH₃ gas, steam or low-grade hydrocarbon such as CH₄ and C₂H₆. The inhibitor in raw material gases can adjust the reactive performance of catalyst to some extent, usually halide or compound containing nitrogen is adopted, wherein the halide can be chloride, bromide, fluoride or iodide such as dichlorethane, chloroethane, ethylene bichloride, vinyl chloride, monochlorobenzene and dichlorobenzene, and nitrogenous compound, e.g nitropropan. Every million shares volume material gas contains 0.1 ~ 20 shares volume of inhibitor.

Activity is an important property of Ag catalyst. Activity means the EO concentration at the reactor outlet at the fixed circumstances (e.g. temp, pressure, air speed etc). That is to say, the lower a certain temp needed for EO concentration, the higher activity the catalyst has; the higher the reaction temperature is, and the lower activity the catalyst has. The activity of catalyst is expressed by the degree of temperature.

The key to this invention is that liquid or gaseous alkaline substance is used to treat $\alpha\text{-Al}_2\text{O}_3$ in certain condition, after alkali treatment, alkalic material e.g. cations of alkali metal and alkaline earth metal and anions e.g. OH⁻ etc do not stay in carrier, through several times' washing, they are removed from the carrier. The aim of alkali treatment is mainly to adjust the carrier surface and inner micropore structure to generate a large number of high energy points on carrier surface and greatly improve the reactive performance of $\alpha\text{-Al}_2\text{O}_3$ as Ag catalyst carrier. Ag and some assistant agents are loaded to carrier during alkali treatment. The loading amount of AG is 5 ~ 40% of catalyst weight, and the assistant can be S, Re, Mo, W, Ni, alkali metals, alkaline earth metals or their mixture. The loading amount of assistant is 0.001 ~ 1% of catalyst weight as counted by element weight. Then Ag catalyst for ethylene epoxidation is made.

The carrier of the Ag catalyst prepared by this invention, through alkali treatment, contains a large number of high energy points on its surface and makes the Ag and assistant catalyst loaded on those high energy points appear higher reactivity. The catalyst is applied in ethylene epoxidation for EO production, in the situation of fixing EO concentration at the reactor outlet, the reaction temperature of catalyst is 10 ~ 20 °C lower than that made by present techniques, and the activity of catalyst is improved greatly and high selectivity is kept at the same time. In addition, fluorochemical is added in the preparation of α - Al_2O_3 carrier in this invention, the selectivity of catalyst prepared by carrier after fluoridizing treatment is higher than that of catalyst prepared by carrier without fluoridizing treatment. As a result, the reactive performances of the whole catalyst are improved and relatively good effects are obtained.

Further explanations are made for this invention through the following examples.

The detailed implementation mode

[Example 1]

1. Preparation of carrier A

500g alumina monohydrate powder material is added into kneading machine, and 125g graphite, 3g calcium-silicate, 160g water are added and fully kneaded and extruded into rasching with external diameter 8mm, inner diameter 4mm and height 6.4mm. It is dried at 120 °C and calcinated at 1500 °C for 4 hours, and then rasching shape α - Al_2O_3 carrier is acquired.

100g α - Al_2O_3 carrier is added into KOH aqueous solution (with 0.05g KOH dissolved in 100ml water) and treated for 10hours at 300 °C. After cooling, deionized water is used to wash the carrier repeatedly until the eluting liquid is neutral, drying at 120 °C.

2. Preparation of catalyst A:

59.1g AgNO_3 is weighted and dissolved in 200ml water. In addition, 26.8g ammonium oxalate is taken and dissolved in 364ml water. The abovementioned two solutions conduct sedimentary reaction at 40 °C, and the acquired silver oxalate sediment is washed with deionized water and filtrated. The filter cake of silver oxalate is washed by ethanediamine aqueous solution composed of 32.8ml ethanediamine and 32.8ml water. 0.115g Cs_2CO_3 and water are added to prepare silver-ammine solution. Carrier A is excessively soaked into the abovementioned silver-ammine solution in vacuum; wet materials are taken out and dried in air. Then it is put into heat decomposer and swept by hot air for 8minutes at 260 °C, after that, it is taken out and catalyst A is acquired. Catalyst A contains 13.0% Ag as counted by weight and 326ppm Cs.

3. The reactive performance test for catalyst A:

10ml micro-reaction evaluation system is adopted, catalyst is broken into 10 ~ 20 mesh, 10ml is taken out and put into the stainless steel reactor with inner diameter of 8mm. The performance test for ethylene epoxidation reaction is done in micro reaction evaluation system, the related reaction conditions are as following:

Raw material molar composition:

C_2H_4 : 28% O_2 : 6.4% CO_2 : 5% Inhibitor: trace N_2 : the rest

Pressure: 2.1 MPa (gauge pressure)

Air-speed: 7000 h⁻¹

EO concentration at outlet: 1.4 mole %

The reaction results of catalyst A for ethylene epoxidation are shown in table 1.

The following applied methods for catalyst performance test in Examples 2 ~ 7 and Comparison Examples 1 ~ 2 are the same with that in example 1, and the reaction results can be seen in table 1.

[Comparison Example 1]

1. Preparation of carrier A₁

500g alumina monohydrate powder material is added into kneading machine, and 125g graphite, 3g calcium-silicate, 160g water are added and fully kneaded and extruded into rasching with external diameter 8mm, inner diameter 4mm and height 6.4mm. It is dried at 120 °C and calcinated at 1500 °C for 4 hours, and then rasching shape α -Al₂O₃ carrier A₁ is acquired.

2. Preparation of catalyst A₁

Do not conduct carrier A₁ with any alkali treatment, prepare catalyst A₁ according to the same method stated in Example 1, and the difference is the change of Cs amount Catalyst A₁ contains 13.0% Ag as counted by weight and 290ppm Cs.

[Example 2]

1. Preparation of carrier B:

100g α -Al₂O₃ carrier in example 1 is added into the Na₂CO₃ aqueous solution (with 50g Na₂CO₃ dissolved in 500ml water) and treated at 300 °C for 10 hours. Cooling down, washing the carrier with deionized water until the eluting liquid is neutral and drying.

2. Preparation of catalyst B

Catalyst B is prepared according to the method stated in example 1, the differences are that carrier A is replaced by carrier B and the amount of Ag and Cs in catalyst is changed. The prepared catalyst B contains 20% Ag as counted by weight and 250ppm Cs.

[Example 3]

1. Preparation of carrier C

900g alumina monohydrate powder material is added into kneading machine, and 225g graphite, 4.5g calcium-silicate, 0.5g ammonium fluoride and 290g water are added and fully kneaded and extruded into rasching with external diameter 8mm, inner diameter 4mm and height 6.4mm. It is dried at 120 °C and calcinated at 1400 °C for 4 hours, and then rasching shape α -Al₂O₃ carrier is acquired.

100g α - Al_2O_3 carrier is added into KOH aqueous solution (with 10g CsOH dissolved in 500ml water) and treated for 2 hours at 500 °C. After cooling, deionized water is used to wash the carrier repeatedly until the eluting liquid is neutral, drying at 120 °C.

2. Preparation of catalyst C

59.1g AgNO_3 is weighted and dissolved in 200ml water. In addition, 26.8g ammonium oxalate is taken and dissolved in 364ml water. The abovementioned two solutions conduct sedimentary reaction at 40 °C, and the acquired silver oxalate sediment is washed with deionized water and filtrated. The filter cake of silver oxalate is washed by ethanediamine aqueous solution composed of 32.8ml ethanediamine and 32.8ml water. 1.5ml 0.0627g/ml perrenic acid solution, 0.0495g $(\text{NH}_4)_2\text{SO}_4$, 0.143g Cs_2CO_3 and water are added together to prepare silver-ammine solution. Carrier C is excessively soaked into the abovementioned silver-ammine solution in vacuum; wet materials are taken out and dried in air. Then it is put into heat decomposer and swept by hot air for 8 minutes at 260 °C, after that, it is taken out and catalyst C is acquired. Catalyst C contains 13.0% Ag as counted by weight, 243ppm Re, and 41.7ppm S and 405ppm Cs.

[Comparison Example 2]

1. Preparation of carrier C_1

900g alumina monohydrate powder material is added into kneading machine, and 225g graphite, 4.5g calcium-silicate, 0.5g ammonium fluoride and 290g water are added and fully kneaded and extruded into rasching with external diameter 8mm, inner diameter 4mm and height 6.4mm. It is dried at 120 °C and calcinated at 1400 °C for 4 hours, and then Rasching shape α - Al_2O_3 carrier C_1 is acquired.

2. Preparation of catalyst C_1

Do not conduct carrier C_1 with any alkali treatment, prepare catalyst C_1 according to the same method stated in Example 3, and the difference is the change of Re, S, Cs amount. Catalyst C_1 contains 13.0% Ag as counted by weight and 215ppm Re, 50.0ppm S and 445ppm Cs.

[Example 4]

1. Preparation of carrier D

100g α - Al_2O_3 carrier in example 3 is added into 200ml 25% ammonia water and treated at 50 °C for 25 hours. Cooling down, washing the carrier with deionized water until the eluting liquid is neutral and drying at 120 °C.

2. Preparation of catalyst D

Catalyst D is prepared according to the method stated in example 3, the differences are that carrier C is replaced by carrier D and the amount of Ag, Re, S and Cs in catalyst is changed. The prepared catalyst D contains 15.0% Ag as counted by weight and 306ppm Re, 81ppm S and 600ppm Cs.

[Example 5]**1. Preparation of carrier E**

400g alumina monohydrate powder material and 200g alumina trihydrate are added into kneading machine, and 90g graphite, 3g calcium-silicate, 6g ammonium fluoride and 190g water are added and fully kneaded and extruded into rasching with external diameter of 8mm, inner diameter of 4mm and height of 6.4mm. It is dried at 100 °C and calcinated at 1460 °C for 4 hours, and then rasching shape α -Al₂O₃ carrier is acquired.

100g α -Al₂O₃ carrier is added into 300g ethanediamine and treated for 20hours at 100 °C. After cooling, deionized water is used to wash the carrier repeatedly until the eluting liquid is neutral, drying at 150 °C.

2. Preparation of catalyst E

Catalyst E is prepared according to the method stated in example 3, the differences are that carrier E is replaced by carrier C, ammonium sulfate is replaced by ammonium molybdate, and the amount of Ag, Re and Cs in catalyst is changed. The prepared catalyst E contains 10.0% Ag as counted by weight and 280ppm Re, 65ppm Mo and 283ppm Cs.

[Example 6]**1. Preparation of carrier F**

600g alumina monohydrate powder material and 600g alumina trihydrate are added into kneading machine, and 300g graphite, 6g calcium-silicate, 24g ammonium fluoride and 380g water are added and fully kneaded and extruded into rasching with external diameter 8mm, inner diameter 4mm and height 6.4mm. It is dried at 120 °C and calcinated at 1460 °C for 4 hours, and then Rasching shape α -Al₂O₃ carrier is acquired.

Takes 100g α -Al₂O₃ carrier, and introduces the mixed gas of NH₃ gas and air at 200 °C, the (molar) ratio of air to NH₃ gas is 5: 1, and air speed is 18 l/h for 10 hours. After cooling, distilled water is used to wash the carrier repeatedly until the eluting liquid is neutral, drying at 150 °C.

2. Preparation of Catalyst F

59.1g AgNO₃ is dissolved in 200ml water. In addition, 26.8g ammonium oxalate is dissolved in 364ml water. The abovementioned two solutions conduct sedimentary reaction at 40 °C, and the acquired silver oxalate sediment is washed with deionized water and filtrated. The filter cake of silver oxalate is washed by ethanediamine aqueous solution composed of 32.8ml ethanediamine and 32.8ml water. 1.8ml 0.0627g/ml perrhenic acid solution, 0.180g tungstic acid, 0.185g Cs₂CO₃ and water are added together to prepare silver-ammine solution. 100g carrier F is excessively soaked into the abovementioned silver-ammine solution in vacuum; wet materials are taken out and dried in air. Then it is put into heat decomposer and swept by hot air for 8minutes at 260 °C. After that, it is taken out and treated for 4 hours in the atmosphere of hydrogen, then catalyst F is acquired. Catalyst F contains 13.0% Ag as counted by weight, 291ppm Re, and 460ppm Wo and 525ppm Cs.

[Example 7]**1. Preparation of carrier G**

100g α -Al₂O₃ carrier in example 5 is added into 200g pyridine and treated at 400 °C for 5 hours. Cooling down, washing the carrier with distilled water until the eluting liquid is neutral and drying at 150 °C.

2. Preparation of catalyst G

Catalyst G is prepared according to the method stated in example 6, the differences are that carrier F is replaced by carrier G, tungstic acid is replaced by ammonium molybdate and ammonium sulfate, and the amount of Ag, Re, and Cs in catalyst are changed. The prepared catalyst G contains 14.0% Ag as counted by weight and 410ppm Re, 92.0ppm Mo, 32.0ppm S and 700ppm Cs.

Table 1 The reaction results of catalysts for ethylene epoxidation

	Catalyst	Selectivity %	Reaction temperature °C
Example 1	A	82.3	215
Comparison 1	A ₁	82.3	225
Example 2	B	86.4	216
Example 3	C	86.3	221
Comparison 2	C ₁	86.1	235
Example 4	D	86.2	225
Example 5	E	86.3	218
Example 6	F	86.1	215
Example 7	G	86.2	223

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[54] 发明名称 乙烯环氧化银催化剂的制备方法

[57] 摘要

本发明涉及一种乙烯环氧化银催化剂的制备方法。主要解决以往技术制得的银催化剂活性还不够高的缺陷。本发明将 α -氧化铝载体用碱性物质进行碱处理，碱处理包括溶液或气体两种方式，碱性物质用量以载体重量百分比计为 0.01 ~ 500%，处理温度 30 ~ 800℃，处理时间 1 ~ 30 小时，碱处理后的载体用水洗涤至流出液为中性，干燥，制成银催化剂载体，在该载体上负载银和选自硫、铈、钼、钨、镍、碱金属或碱土金属中至少一种的助剂，银的负载量以银计为催化剂重量的 5 ~ 40%，助剂以元素重量计的负载量为催化剂重量的 0.001 ~ 1%。本发明方法制备的银催化剂用于生产环氧乙烷，具有反应温度低、反应活性高的优点，同时保持催化剂的高选择性。可用于生产环氧乙烷的银催化剂工业生产中。

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1、一种乙烯环氧化银催化剂的制备方法，依次包括以下步骤：

a) 以 α -氧化铝为载体，载体用量为催化剂重量的 60~94%；

b) 用碱性物质对载体进行碱处理，包括使用碱性物质溶液或气体两种处理方式，碱性物质用量以载体重量百分比计为 0.01~500%，处理温度 30~800℃，处理时间 1~30 小时，碱处理后的载体用水洗涤至流出液为中性，干燥，得到银催化剂载体；

c) 在 b 步骤制得的载体上负载银，银的负载量以银计为催化剂重量的 5~40%；

d) 在负载银之前、同时或之后负载助催化剂，助催化剂可以选自硫、铈、钼、钨、镍、碱金属、碱土金属中的一种或它们的混合物，助催化剂以元素重量计的负载量为催化剂重量的 0.001~1%。

2、根据权利要求 1 所述乙烯环氧化银催化剂的制备方法，其特征在于碱性物质包括无机碱性化合物、有机碱性化合物或它们的混合物。

3、根据权利要求 2 所述乙烯环氧化银催化剂的制备方法，其特征在于无机碱性化合物可以是碱金属或碱土金属的氧化物、氢氧化物、弱酸盐或它们的混合物。

4、根据权利要求 2 所述乙烯环氧化银催化剂的制备方法，其特征在于无机碱性化合物为氨，可以是氨水、氨气、氨气和空气的混合气或氨气和氮气的混合气。

5、根据权利要求 2 所述乙烯环氧化银催化剂的制备方法，其特征在于有机碱性化合物为可以是胺类化合物、吡啶类化合物或它们的混合物。

6、根据权利要求 2 所述乙烯环氧化银催化剂的制备方法，其特征在于碱性物质用量以载体重量百分比计为 0.05~300%。

7、根据权利要求 3 所述乙烯环氧化银催化剂的制备方法，其特征在于处理温度为 50~500℃，处理时间为 2~20 小时。

8、根据权利要求 1 所述乙烯环氧化银催化剂的制备方法，其特征在于碱金属为锂、钠、钾或铯，碱土金属为镁或钙。

9、根据权利要求 1 所述乙烯环氧化银催化剂的制备方法，其特征在于 a 步骤的制备，在原料中还加入含氟化合物，含氟化合物的加入量以氟计为氧化铝重量的 0.01~20%，然后捏合、成型、焙烧。

乙烯环氧化银催化剂的制备方法

技术领域

本发明涉及一种用于乙烯环氧化银催化剂的制备方法。

背景技术

银催化剂用于乙烯环氧化生产环氧乙烷已在工业装置广泛实施，高活性和高选择性是银催化剂的两个重要性能，而载体性能对银催化剂活性、选择性起着至关重要的作用。银催化剂通常以 α -氧化铝为载体，以银作为主要活性组份，添加少量助催化剂制备得到。要获得高活性催化剂，必须提供高的银粒比表面，要求载体具有足够大的比表面，但比表面过大，会导致反应系统撤热困难，加剧反应深度氧化，降低产物环氧乙烷选择性。如何协调催化剂活性和选择性的关系，使催化剂同时具有高的活性和高选择性，一直是人们长期关注研究的重点。现有技术中，许多专利涉及生产环氧乙烷的银催化剂及催化剂载体，虽然目前设计的银催化剂及载体已进行了充分改进，具有较高的活性和选择性，但考虑到环氧乙烷生产规模，催化剂活性或选择性稍有提高，都会带来很高的经济效益，因此，现有技术中仍有开发更高活性、选择性银催化剂的需求。

US4742034 介绍了一种乙烯环氧化反应的银催化剂制备方法，使用富含碱金属的氧化铝载体，主体中加入碱金属和氟，碱金属主要以氟化物或硝酸盐的形式引入，该催化剂具有较好的选择性和稳定性，含氟催化剂选择性达到 81.2%，比不含氟催化剂选择性提高 2%。

EP716884A₂ 介绍了一种银催化剂制备方法，在载体中预浸渍碱金属，经热处理，使之负载到载体上，然后主体浸渍银、铈、硫、碱金属等，载体预处理的目的是提高催化剂的初始选择性和选择性的稳定性，如此得到的催化剂用于乙烯环氧化反应，选择性达到 82%，并具有长期稳定的选择性。

中国专利 95196582.4 (CN1168644A) 提供了一种用于乙烯氧化为环氧乙烷银催化剂的制备方法，将惰性载体浸渍在一种银/胺溶液中，经过焙烧后，引入 Cs、Re、S 等助催化剂，于 100℃ 以上惰性气氛中煅烧。由 O₂7%(V)、8%CO₂、15%C₂H₄、70%N₂ 组成的原料混合物以 5500h⁻¹ 空速通过催化剂，反应压力 21.69 巴，当环氧乙烷流出浓度为 1.5% (体

积)时,体现催化剂活性的反应温度为 228~259℃,选择性为 81~83.7%。

中国专利 00119774.6 介绍了一种银催化剂载体的制备方法,在氧化铝原料中加入含氟化合物,高温焙烧,生成 α -氧化铝,然后与制孔剂、粘结剂等添加剂捏合、成型,经过第二次高温焙烧制得 α -氧化铝载体,用该载体制备的银催化剂,用于乙烯环氧化制备环氧乙烷反应,具有较高的选择性,但催化剂反应活性还不够高,在反应压力 2.1MPa(表压)、空速 7000 小时⁻¹条件下,当反应器出口环氧乙烷浓度为 1.4 摩尔%时,体现催化剂活性的反应温度为 225~230℃。

上述催化剂均具有较好的选择性、活性和稳定性,但催化剂反应活性还不够高。

发明内容

本发明所要解决的技术问题是克服现有文献制得的银催化剂反应活性还不够高的缺陷,提供一种乙烯环氧化银催化剂的制备方法,该方法制备的催化剂用于乙烯环氧化反应生产环氧乙烷,具有反应温度低、反应活性高的优点,同时保持催化剂的高选择性。

为解决上述技术问题,本发明采用的技术方案如下:一种乙烯环氧化银催化剂的制备方法,依次包括乙烯步骤:

- a)以 α -氧化铝为载体,载体用量为催化剂重量的 60~94%;
- b)用碱性物质对载体进行碱处理,包括使用碱性物质溶液或气体两种处理方式,碱性物质用量以载体重量百分比计为 0.01~500%,处理温度 30~800℃,处理时间 1~30 小时,碱处理后的载体用水洗涤至流出液为中性,干燥,得到银催化剂载体;
- c)在 b 步骤制得的载体上负载银,银的负载量以银计为催化剂重量的 5~40%;
- d)在负载银之前、同时或之后负载助催化剂,助催化剂可以选自硫、铈、钼、钨、镍、碱金属、碱土金属中的一种或它们的混合物,助催化剂以元素重量计的负载量为催化剂重量的 0.001~1%。

上述技术方案中,制备 α -氧化铝载体以水合氧化铝、过渡相氧化铝或二者的混合物为原料,考虑到原料成本问题,所用氧化铝原料最好选用水合氧化铝,可以是一水氧化铝、假一水氧化铝、三水氧化铝或无定形铝胶中的一种,也可以是其中两种或两种以上的混合物,优选一水氧化铝、三水氧化铝或二者混合物。

由于氟化物有利于氧化铝在焙烧中转化成 α -氧化铝晶体,消除不必要的微孔,提高载体作为催化剂的选择性。本发明制备 α -氧化铝载体时,在氧化铝原料中加入粘结剂、致孔剂和水,同时可以非强制性加入一种含氟化合物,得到混和物料;其中含氟化合物的

加入量以氟计为氧化铝重量的 0.01~20%，粘结剂加入量为氧化铝重量的 0.01~10%，致孔剂加入量为氧化铝重量的 5~50%；使用的含氟化合物包括碱金属氟化物、碱土金属氟化物、 NH_4F 、 $(\text{NH}_4)\text{HF}_2$ 、 AlF_3 或 HF 等等，优选采用氟化铵、氟化氢或氟化铝；使用的粘结剂包括硝酸、铝胶、无机粘土、硅酸镁、硅酸钙、硅酸钡、铝酸钡、纤维素、甲基或乙基或羧乙基纤维素、硬脂酸甲酯或乙酯、蜡类、聚烯烃氧化物等；合适的致孔剂包括含碳材料，如焦炭、碳粉、石墨；粉末塑料如聚乙烯、聚苯乙烯、聚碳酸酯、松香；纤维素和纤维素系材料；木屑和其它植物材料如粉末状硬壳如山核桃壳、胡桃壳、榛壳等。

将上述混和物料充分捏合后，制成一定的形状，载体形状可以是球状、块状、丸状、圆柱状、拉西环状、多孔圆柱状、三叶草状等。把上述成型物于 60—200℃干燥，再经过高温焙烧，即得到经氟处理或不经氟处理的 α -氧化铝载体。所述焙烧温度为 1000℃—1700℃，优选范围 1200℃—1600℃，更好优选范围 1300℃—1500℃，焙烧时间为 0.5—20 小时，优选范围 1—10 小时，更好优选范围 1—6 小时。有时，也可以通过用不同粒度的 α -氧化铝粉末混和的方法来控制载体的孔分布。

氟处理后的氧化铝，经高温焙烧具有片状晶体构型，通过选取合适的起始氧化铝原料和加入的含氟化合物含量，可以控制片状晶体宽度为 0.1—30 微米，优选范围为 0.5—10 微米；厚度为 0.1—4 微米，优选范围为 0.1—2 微米。

将制得的 α -氧化铝载体(包括经氟处理或不经氟处理)用碱性物质进行碱处理，使用的碱性物质包括所有可配制成碱性溶液的化合物及呈碱性的气体，例如无机碱性化合物、有机碱性化合物或它们的混合物，其中无机碱性化合物可以选自碱金属或碱土金属的氧化物、氢氧化物，选自碱金属或碱土金属的弱酸盐，如碳酸盐、醋酸盐、草酸盐、羧酸盐或它们的混合物，所述的碱金属优选锂、钠、钾或铯，碱土金属优选镁或钙；无机碱性化合物也可以选用氨，氨可以采用氨水和氨气两种物态；有机碱性化合物选自胺类化合物、吡啶类化合物或它们的混合物，胺类化合物如乙二胺、乙醇胺、甲胺、乙胺、苯胺或其混合物，优选乙二胺、乙醇胺或其混合物，吡啶类化合物如吡啶、三甲基吡啶等；碱性物质用量以载体重量百分比计为 0.01~500%，优选 0.05~300%，处理温度 30~800℃，优选 50~500℃，更加优选 80~400℃，处理时间 1~30 小时，优选 2~20 小时，一般来说处理温度越高，处理时间越短。

碱处理方式可以采用碱性物质溶液或气体两种物态方式进行处理，用碱性物质溶液处理时，溶液的配制是将以载体重量百分比计为 0.01~500%的碱性物质溶解在水、甲醇、乙醇、丙酮或氯仿等溶剂中，溶剂优先选用水或乙醇，使配制的溶液体积至少能够浸湿载

体, 溶液与载体的体积比可以是 0.1~20:1, 优选 1~5:1, 使用的具体碱性物质溶液可以是: 氢氧化锂水溶液、氢氧化钠甲醇溶液、氢氧化钾水溶液、氢氧化铯乙醇溶液、氨水、碳酸钠水溶液、乙二胺、乙醇胺、吡啶或三甲基吡啶等; 用碱性物质气体处理时, 所用的气体可以是氨气、氨气和空气的混合气或氨气和氮气的混合气, 其中空气(或氮气): 氨气的摩尔比为 0~10:1, 使气体以一定速率通过载体床层, 处理时间为 1~30 小时, 碱气体通入量以载体重量百分比计为 0.01~500%。

碱处理后的载体用水反复多次洗涤, 水可以是蒸馏水或脱离子水, 直至洗涤流出液显示中性, 于 80~200℃下干燥, 即得到生产环氧乙烷的银催化剂载体。通过上述方法得到的载体, 其比表面积一般为 0.2~1.5 米²/克, 吸水率一般为 0.2~0.8 毫升/克, 堆比重一般为 0.4~1.0 克/毫升。

本发明催化剂制备中, 将银负载在碱处理的载体上的方法有多种, 可以用硝酸银水溶液浸渍载体, 然后用氢、肼或甲醛把银离子还原成金属银; 也可用草酸银或碳酸银的氨水溶液浸渍载体, 干燥, 经加热使银离子还原成金属银。最好的方法是用一种银盐—有机溶剂/还原剂—水的混合物作为银浸渍液, 浸渍载体后, 经热处理使银离子还原成金属银, 这种方法能使金属银以高度分散的细颗粒状负载于载体之上。

作为银浸渍液的银盐—有机溶剂/还原剂—水的混合物, 其中的银盐包括无机盐和有机盐, 如硝酸银、碳酸银、硫酸银、氯化银、草酸银、乙酸银、乳酸银、丁二酸银、乙醇酸银, 优选草酸银。有机溶剂/还原剂既可以作为银盐的溶剂, 同时又可以在加热的情况下把离子态的银还原成金属态的银, 可以采用有机胺类, 尤其是链烷醇胺、亚烷基二胺, 如乙二胺、丙二胺、乙醇胺、丙醇胺、丁醇胺以及它们的混合物或它们与氨的混合物。银浸渍液常用的配制方法有两种, 可以通过以下两个例子来说明。一个例子是把氧化银与乙二胺和草酸的混合物进行反应, 生成一种含草酸银—乙二胺的混合物作为银浸渍液, 注意避免把氧化银直接加入到乙二胺, 因为由此生成的银—乙二胺溶液不稳定, 容易引起爆炸。另一个例子是: 把硝酸银溶液和草酸铵溶液混合, 生成草酸银沉淀, 反复洗涤所得的沉淀, 以洗去其中的硝酸根, 然后用乙二胺水溶液溶解草酸银沉淀, 所得的草酸银—乙二胺的混合物可作为银浸渍液。

将载体从银浸渍液中取出, 甩干, 进行热处理, 热气体流过湿载体, 除去湿载体中的有机溶剂和水, 同时使银以金属细颗粒状沉积在载体上, 银的负载量为催化剂重量的 5~40%, 优选 10~20%。热处理气体可以是空气、氮气、氧气、氢气、二氧化碳、蒸汽或它们的混合物。热处理温度可以选用 80~700℃, 优选 150~500℃。热处理时间可以选用

1 分钟~10 小时, 优选为 2~30 分钟。

助催化剂可以有效地改善银催化剂的催化性能, 如选择性、活性、稳定性等性能。本发明方法选用的助催化剂选自硫、铯、钼、钨、镍、碱金属、碱土金属中的一种或它们的混合物, 优选硫、铯、碱金属或它们的混合物, 助催化剂以元素重量计的负载量为催化剂重量的 0.001~1%, 优选 0.003~0.1%; 其中碱金属是一类最常用的助催化剂, 以铯为最佳, 适用的碱金属助催化剂原料的实例有, 碱金属的硝酸盐、氢氧化物、碳酸盐、草酸盐、羧酸盐、醇盐或它们的混合物, 具体实例有碳酸铯、硝酸铷、氢氧化钾、乙酸钠、草酸锂。助催化剂可以在银浸渍于载体之前、同时或之后施加到载体上。

本发明方法制备的催化剂用于乙烯和分子氧反应生产环氧乙烷。所采用的工艺条件与通常文献中所记载的工艺条件相近。本发明银催化剂可以采用的工艺条件为: 反应温度在 150~300℃, 最好在 200~280℃; 反应压力在 10~40 千克/平方厘米, 最好在 15~30 千克/平方厘米; 气体空间速率在 1000~30000 小时⁻¹, 更好在 3000~15000 小时⁻¹。原料气的体积组成可以为: 0.5~40% 的乙烯, 3~10% 的氧气; 5~30% 的二氧化碳, 少量的抑制剂, 其余为不活泼气体, 如氮气、氩气、水蒸汽或低级碳氢化合物, 如甲烷、乙烷。原料气中的抑制剂可以在一定范围内调节催化剂的反应性能, 通常采用卤化物或含氮化合物, 卤化物可以是氯化物、溴化物、氟化物或碘化物, 例如二氯乙烷、氯乙烷、二氯乙烯、氯乙烯、一氯代苯、二氯代苯。含氮化合物如硝基丙烷。每百万份体积的原料气中含 0.1~20 份体积的抑制剂。

活性是银催化剂的重要性能。活性是指固定其它反应条件(如温度、压力、空速等)的情况下, 反应器出口处环氧乙烷浓度的高低, 也就是说, 如果达到某一确定的环氧乙烷浓度所需要的温度越低, 催化剂的活性就越高; 反应温度越高, 则说明催化剂的活性越低。催化剂的活性用反应温度的高低来表示。

本发明方法的关键在于用液态或气态的碱性物质在一定条件下对 α -氧化铝载体进行碱处理, 碱处理后载体所含的碱性物质如碱金属、碱土金属等阳离子及 OH⁻等阴离子并不留在载体中, 通过多次洗涤将其从载体中除去, 碱处理的目的是主要微观调节载体表面及内部微孔结构, 使载体表面产生大量高能位点, 有效改善 α -氧化铝作为银催化剂载体的反应性能。在碱处理载体上负载银和一些助剂, 银的负载量为催化剂重量的 5~40%, 助剂可以是 S、Re、Mo、W、Ni、碱金属、碱土金属或它们的混合物, 助剂以元素重量计的负载量为催化剂重量的 0.001~1%, 制得本发明乙烯环氧化银催化剂。

本发明方法制备的银催化剂, 通过将催化剂的载体经过碱处理, 使载体表面富含大量

高能位点,使得负载在这些高能位点上的银和助催化剂比通常显现更高的反应活性,该催化剂用于乙烯环氧化反应生产环氧乙烷,在固定反应器出口环氧乙烷浓度的情况下,催化剂的反应温度比现有技术降低 10~20℃,催化剂的活性得到了显著提高,同时保持催化剂的高选择性。另外,本发明在 α -氧化铝载体制备中加入含氟化合物,经氟处理载体制备的催化剂选择性比不经氟处理载体制备的催化剂选择性有所提高,从而提高了整个催化剂的反应性能,取得了较好效果。

下面通过实施例对本发明作进一步的阐述。

具体实施方式

【实施例 1】

1、制备载体 A:

取一水氧化铝粉料 500 克置于捏和机中,加入石墨 125 克、硅酸钙 3 克,水 160 克,充分捏和,挤压成外径 8 毫米,内径 4 毫米,高 6.4 毫米的拉西环。120℃烘干,1500℃焙烧 4 小时,得到拉西环状 α -氧化铝载体。

取 α -氧化铝载体 100 克,加入氢氧化钾水溶液(0.05 克氢氧化钾溶于 100 毫升水),于 300℃处理 10 小时。冷却后,用去离子水反复洗涤载体至流出液为中性,于 120℃干燥。

2、制备催化剂 A:

称取硝酸银 59.1 克溶于 200 毫升水中。另取草酸铵 26.8 克溶于 364 毫升水中。上述两溶液在 40℃下进行沉淀反应,将得到的草酸银沉淀用去离子水洗涤,过滤。将草酸银滤饼用 32.8 毫升乙二胺和 32.8 毫升水的乙二胺水溶液溶解。加入碳酸铯 0.115 克,再加水,制成银胺络合液。将载体 A 在真空下过量浸渍上述的银胺络合液,捞出湿料沥干,放入热分解器中,用 260℃热空气吹扫 8 分钟,取出,得催化剂 A。催化剂 A 以重量计含 13.0% 的银,326ppm 的铯。

3、催化剂 A 的反应性能测试:

采用 10 毫升微型反应评价系统,把催化剂破碎至 10~20 目,取 10 毫升装入内径为 8 毫米的不锈钢反应器中,在微型反应评价系统中进行乙烯环氧化反应性能测试,有关反应条件如下:

原料气摩尔组成:

C₂H₄: 28% O₂: 6.4% CO₂: 5% 抑制剂: 微量 N₂: 其余

压力: 2.1MPa(表压)

空速: 7000 小时⁻¹

出口环氧乙烷浓度: 1.4 摩尔%

催化剂 A 的乙烯环氧化反应结果见表 1。

以下实施例 2~7、比较例 1~2 制备的催化剂性能测试方法与实施例 1 的性能测试方法相同, 反应结果见表 1。

【比较例 1】

1、制备载体 A₁:

取一水氧化铝粉料 500 克置于捏和机中, 加入石墨 125 克、硅酸钙 3 克, 水 160 克, 充分捏和, 挤压成外径 8 毫米, 内径 4 毫米, 高 6.4 毫米的拉西环。120℃烘干, 1500℃焙烧 4 小时, 得到拉西环状 α-氧化铝载体 A₁。

2、制备催化剂 A₁:

载体 A₁ 不用任何碱性物质处理, 按照与实施例 1 相同的方法制备催化剂 A₁, 不同的是改变铯的用量, 催化剂 A₁ 以重量计含 13.0% 的银, 290ppm 的铯。

【实施例 2】

1、制备载体 B:

取实施例 1 的 α-氧化铝载体 100 克, 加入碳酸钠水溶液 (50 克碳酸钠溶于 500 毫升水中), 于 300℃下处理 10 小时。冷却、用去离子水反复洗涤载体至流出液为中性, 干燥。

2、制备催化剂 B:

按实施例 1 的方法制备催化剂 B, 不同的是用载体 B 代替载体 A, 改变催化剂中银和铯的用量, 制得的催化剂 B 以重量计含 20% 的银, 250ppm 的铯。

【实施例 3】

1、制备载体 C:

取一水氧化铝粉料 900 克置于捏和机中, 加入石墨 225 克、硅酸钙 4.5 克, 氟化铵 0.5 克, 水 290 克, 充分捏和, 挤压成外径 8 毫米, 内径 4 毫米, 高 6.4 毫米的拉西环。120℃烘干, 1400℃焙烧 4 小时, 得到拉西环状 α-氧化铝载体。

取 α-氧化铝载体 100 克, 加入氢氧化铯乙醇溶液 (10 克氢氧化铯溶于 500 毫升乙醇

中)，于 500℃下处理 2 小时，冷却、用去离子水反复洗涤载体至流出液为中性，120℃干燥。

2、制备催化剂 C：

取 59.1 克硝酸银溶于 200 毫升水中。另取草酸铵 26.8 克溶于 364 毫升水中。上述两溶液在 40℃下进行沉淀反应，将得到的草酸银沉淀用去离子水洗涤，过滤。将草酸银滤饼用 32.8 毫升乙二胺和 32.8 毫升水的乙二胺水溶液溶解。加入浓度为 0.0627 克/毫升的高铈酸溶液 1.5 毫升，硫酸铵 0.0495 克，碳酸铯 0.143 克，再加水，制成银胺络合液。将载体 C 在真空下过量浸渍上述的银胺络合液，捞出湿料沥干，放入热分解器中，用 260℃热空气吹扫 8 分钟，取出，得催化剂 C。催化剂 C 以重量计含 13.0%的银，243ppm 的铈，41.7ppm 的硫，405ppm 的铯。

【比较例 2】

1、制备载体 C₁：

取 α-氧化铝粉料 900 克置于捏和机中，加入石墨 225 克、硅酸钙 4.5 克，氟化铵 0.5 克，水 290 克，充分捏和，挤压成外径 8 毫米，内径 4 毫米，高 6.4 毫米的拉西环。120℃烘干，1400℃焙烧 4 小时，得到拉西环状 α-氧化铝载体 C₁。

2、制备催化剂 C₁：

载体 C₁ 不用任何碱性物质处理，按照与实施例 3 相同方法制备催化剂 C₁，不同的是改变铈、硫、铯的用量，催化剂 C₁ 以重量计含 13.0%的银，215ppm 的铈，50.0ppm 的硫，445ppm 的铯。

【实施例 4】

1、制备载体 D：

取实施例 3 的 α-氧化铝载体 100 克，加入重量浓度为 25%的浓氨水 200 毫升，于 50℃下处理 25 小时，冷却、用去离子水反复洗涤载体至流出液为中性，120℃干燥。

2、制备催化剂 D：

按实施例 3 的方法制备催化剂 D，不同的是用载体 D 代替载体 C，改变催化剂中银、铈、硫、铯的用量，制得的催化剂 D 以重量计含 15.0%的银，306ppm 的铈，81ppm 的硫，600ppm 的铯。

【实施例 5】**1、制备载体 E:**

取一水氧化铝粉料 400 克和三水氧化铝粉料 200 克置于捏和机中, 加入石墨 90 克、硅酸钙 3 克, 氟化铵 6 克, 水 190 克, 充分捏和, 挤压成外径 8 毫米, 内径 4 毫米, 高 6.4 毫米的拉西环。100℃烘干, 1460℃焙烧 4 小时, 得到拉西环状 α -氧化铝载体。

取 α -氧化铝载体 100 克, 加入乙二胺 300 克, 在 100℃下处理 20 小时。冷却后, 用蒸馏水反复洗涤载体至流出液为中性, 于 150℃干燥。

2、制备催化剂 E:

按实施例 3 的方法制备催化剂 E, 不同的是用载体 E 代替载体 C, 用钼酸铵代替硫酸铵, 改变催化剂中银、铈、铈的用量, 制得的催化剂 E 以重量计含 10.0%的银, 280ppm 的铈, 65ppm 的钼, 283ppm 的铈。

【实施例 6】**1、制备载体 F:**

取一水氧化铝粉料 600 克和三水氧化铝粉料 600 克置于捏和机中, 加入石墨 300 克、6 克硅酸钙, 24 克氟化铵, 水 380 克, 充分捏和, 挤压成外径 8 毫米, 内径 4 毫米, 高 6.4 毫米的拉西环。120℃烘干, 1460℃焙烧 4 小时, 得到拉西环状 α -氧化铝载体。

取 100 克 α -氧化铝载体, 于 200℃下通入氨气和空气的混合气体, 空气:氨气(摩尔)比为 5:1, 空速 18 升/小时, 保持 10 小时。冷却后, 用蒸馏水反复洗涤载体至流出液为中性, 于 150℃干燥。

2、制备催化剂 F:

取 59.1 克硝酸银溶于 200 毫升水中。另取草酸铵 26.8 克溶于 364 毫升水中。上述两溶液在 40℃下进行沉淀反应, 将得到的草酸银沉淀用去离子水洗涤, 过滤。将草酸银滤饼用 32.8 毫升乙二胺和 32.8 毫升水的乙二胺水溶液溶解, 加入浓度为 0.0627 克/毫升的高铈酸 1.8 毫升, 钨酸 0.180 克, 再加入碳酸铈 0.185 克, 再加水, 制成银胺络合液。取 100 克载体 F 在真空下过量浸渍上述的银胺络合液, 捞出湿料沥干, 放入热分解器中, 用 260℃热空气吹扫 8 分钟, 取出, 在氢气氛下 400℃处理 4 小时, 得催化剂 F。催化剂 F 以重量计含 13.0%的银, 291ppm 的铈, 460ppm 的钨, 525ppm 的铈。

【实施例 7】**1、制备载体 G:**

取实施例 6 的 α -氧化铝载体 100 克, 加入吡啶 200 克, 于 400℃ 下处理 5 小时。冷却后, 用蒸馏水反复洗涤载体至流出液为中性, 于 150℃ 干燥。

2、制备催化剂 G:

按实施例 6 的方法制备催化剂 G, 不同的是用载体 G 代替载体 F, 用钼酸铵、硫酸铵代替钨酸, 改变催化剂中银、铈、铈的用量, 制得的催化剂 G 以重量计含 14.0% 的银, 410ppm 的铈, 92.0ppm 的钼, 32.0ppm 的硫, 700ppm 的铈。

表 1 催化剂的乙烯环氧化反应结果

	催化剂	选择性%	反应温度℃
实施例 1	A	82.3	215
比较例 1	A ₁	82.3	225
实施例 2	B	86.4	216
实施例 3	C	86.3	221
比较例 2	C ₁	86.1	235
实施例 4	D	86.2	225
实施例 5	E	86.3	218
实施例 6	F	86.1	215
实施例 7	G	86.2	223